DECLARATION

I, Tomoko Drummond, a staff member of HIROTA, NAGARE & ASSOCIATES, 4th Floor, Shinjuku TR Bldg., 2-13, Yoyogi 2-chome, Shibuya-ku, Tokyo 151-0053, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the following is a true and correct translation made by me into the English language of the accompanying copy of the document in respect of Japanese Patent Application No. 2001-059113 filed on March 2, 2001 in the name of RICOH COMPANY, LTD.

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[TITLE OF THE INVENTION] CARRIER FOR DEVELOPER FOR DEVELOPING ELECTROSTATIC LATENT IMAGE, TONER USING SAME AND IMAGE FORMING METHOD USING SAME
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[TITLE OF THE INVENTION]

CARRIER FOR DEVELOPER FOR DEVELOPING ELECTROSTATIC LATENT IMAGE, TONER USING SAME AND IMAGE FORMING METHOD USING SAME

[SCOPE OF CLAIMS]

[Claim 1] A carrier for a developer for developing an electrostatic image, comprising a coating layer, the coating layer comprising a coating resin and carbon particles having a number average particle diameter of 0.01-0.1 μm.

[Claim 2] A carrier as claimed in claim 1, wherein the carrier has a weight average particle diameter of 25-65 μm and such a particle diameter distribution that that portion of said carrier having a particle diameter of less than 37 μm but no less than 26 μm accounts for 1-60% of a total weight of said carrier.

[Claim 3] A toner comprising the carrier for a developing an electrostatic image according to claim 1 or 2, wherein said toner is used in an image forming method which comprises the steps of:

developing an latent image formed on an image forming member with the toner of a developing member to form a toner image on said image forming member;

transferring said toner image to a transfer member;

collecting the toner and the carrier remaining on said image forming member after the transferring step; and

recycling the collected toner and the carrier for use in the contacting

step.

[Claim 4] An image forming method, comprising the steps of:

developing an latent image formed on an image forming member with the toner according to claim 3 of a developing member to form a toner image on said image forming member;

transferring said toner image to a transfer member;

collecting the toner and the carrier remaining on said image forming member after the transferring step; and

recycling the collected toner and the carrier for use in the contacting step.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field Pertinent to the Invention]

The present invention is related to a coated carrier for dry two-component developer, a toner and an image forming method.

[0002]

[Prior Art]

Conventionally a cascade development method as disclosed in U.S. Pat. No. 2,618,552 and a magnetic brush development method as disclosed in U.S. Pat. No. 2,874,063 are known as methods for developing latent electrostatic images to visible images by use of toner. In any of these development methods, a dry two-component developer is employed. Such a dry two-component developer is composed of relatively large carrier particles and fine toner particles which are triboelectrically held on the surface of the relatively large carrier

particles by the electric force generated by the friction between the carrier particles and toner particles. When such a dry two-component developer is brought into contact with latent electrostatic images, the toner particles are attracted to the latent electrostatic images, with the bonding force between the carrier particles and the toner particles being overcome by the attracting force of the electric field formed by the latent electrostatic images for bringing the toner particles towards the electrostatic images, so that the toner particles are deposited on the latent electrostatic images, whereby the latent electrostatic images are developed to visible toner images. For the above-mentioned development, it is necessary that the toner particles by provided with accurate chargeability and charge quantity so as to be selectively attracted to the desired image area formed on a photoconductor.

[0003]

In conventional developers, during the process of making a number of copies, there takes place so-called "spent phenomenon" that a toner film is formed on the surface of the carrier particles as a result of collision between the toner particles and the carrier particles and collision between such developer particles and mechanical portions of a development unit, so that the charging performance of the carrier particles is decreased. This will result in deposition of the toner particles on the background of the images and of lowering of the copy quality. When the filming phenomenon excessively develops, there occurs the case where the developer must be exchanged with fresh one in its entirety, which will lead to an increase in the copy making cost.

[0004]

To cope with the spent phenomenon, various methods have been proposed in which surfaces of carrier particles are coated with a resin having low surface energy. These methods, however, are not fully satisfactory. For example, a carrier coated with a styrene resin, a methacrylate copolymer resin or a styrene resin, which has a relatively high critical surface tension, still causes a spent phenomenon upon repeated use, though the charging characteristics thereof are good. A polyterafluoroethylene resin, which has a low critical surface tension, can improve the spent carrier problem. However, since a polytetrafluoroethylene resin is located on the most negative side of the turboelectric series, it is ill-suited for use in a developer in which the toner is to be negatively charged.

[0005]

Because of its low surface energy, a silicone resin is also proposed as a coating resin for carriers with a view toward the prevention of the spent-carrier problems (Japanese Examined Patent Publication No. S44-27879 and Japanese Laid Open Patent Publication No. S50-2543). While the use of a silicone resin can prevent toner deposition onto carrier surface, it has a problem because the mechanical strengths thereof such as water resistance and impact resistance are not sufficient. Thus, as upon repeated collision between such developer particles and mechanical portions of a development unit, the silicone resin coating is gradually worn so that the carrier core is exposed on the surface the carrier. As a consequence, the turboelectric characteristics of

the carrier becomes so unstable that the image quality produced is lowered. Additionally, carriers having a resin coating have a large resistivity and are apt to cause the so-called edge effect (a phenomenon that image density of a center part of a large solid image is lighter than that of an edge part thereof) in developed images, resulting in deterioration of the reproducibility of solid images and half-tone images.

[0006]

In an attempt to solve the above problems, there is a proposal to incorporate an electroconductive material into a resin layer of carrier particles so as to reduce the electric resistivity thereof. The carrier particles imparted with a suitable degree of the electrical conductivity can serve to provide developing electrodes so that the development of an electrostatic latent image can be conducted while maintaining close contact between the electrode and the latent image. By this expedience, not only line images but also large solid images can be reproduced with good fidelity. As the electroconductive material, the use of carbon has been proposed. However, the conventional carrier having a carbon-containing resin coating has a problem that carrier deposition is not effectively prevented when the particle size of the carrier is small.

[0007]

As for developers, the use of a small size toner will greatly improve the reproducibility of dot images but, in this case, occurrence of background stains and reduction of color density are caused due to the fact that the small size toner has a large surface area to be charged. To improve charging efficiency of a small size toner, the use of a small size

carrier has been proposed (Japanese Laid Open Publication No. H06-332237 and Japanese Patent Nos. 2703917 and 2769894).

[0008]

The use of a small size carrier will give the following merits. Because of a large surface area, every toner can be sufficiently charged by friction so that the formation of a low charging amount toner or a reversed charge toner can be minimized. Thus, background stains and toner dispersion or blurs of a dot image can be reduced so that the dot image reproducibility is improved. Further, it is possible to reduce average charging amount of the toner. As a consequence, a high image density is obtainable. The use of a small size carrier can thus compensate demerits of a small size toner and is effective for obtaining desired properties of the small size toner.

[0009]

The known small size carriers, however, have the following problems. In a developing stage for developing an electrostatic image on a photoconductor drum, a carrier is magnetically held by a developing cylinder so that the carrier is not transferred to the photoconductor drum. When the particle size of the carrier is small, however, the degree of magnetization per unit weight is so small that the carrier is easily released from the magnetic field of the developing cylinder and is trapped by the photoconductor drum (phenomenon of carrier deposition or carrier attraction). Such carrier deposition occurs more frequently as the particle size of the carrier becomes small. As the carrier deposition proceeds, the amount of the carrier in the developing zone decreases.

This will result in failure to sufficiently charge the toner so that background steins of images and scattering of toner particles from the developing device may occur.

[0010]

[Problem to be Solved by the Invention]

It is, therefore, an object of the present invention is to solve the above-mentioned problems in the conventional art, and to provide a carrier for an image developer for electrophotography, inhibiting problems related to carrier depositions in spite of its small particle size, and maintaining stable quality in terms of electric resistance. Another object of the present invention is to provide a toner containing such carrier, an image forming method using such toner, and especially an image forming method in which a total amount of carrier in a developing device is maintained at a certain level.

[0011]

[Means for Solving the Problem]

Means for solving the aforementioned problems are as follows.

The first aspect of the present invention is a carrier for a developer for developing an electrostatic image, which comprises a coating layer, the coating layer comprising a coating resin and carbon particles having a number average particle diameter of 0.01-0.1 μm.

[0012]

The second aspect of the present invention is a carrier as in the first aspect, wherein the carrier has a weight average particle diameter of 25-65 μm and such a particle diameter distribution that that portion of said carrier having a particle diameter of less than 37 μm but no less than 26 μm accounts

for 1-60% of a total weight of said carrier.

[0013]

The third aspect of the present invention is a toner which comprises the carrier for a developing an electrostatic image according to the first or second aspect, wherein said toner is used in an image forming method which comprises the steps of:

developing an latent image formed on an image forming member with the toner of a developing member to form a toner image on said image forming member;

transferring said toner image to a transfer member;

collecting the toner and the carrier remaining on said image forming member after the transferring step; and

recycling the collected toner and the carrier for use in the contacting step.

[0014]

The fourth aspect of the present invention is an image forming method, which comprises the steps of:

developing an latent image formed on an image forming member with the toner according to the third aspect of a developing member to form a toner image on said image forming member;

transferring said toner image to a transfer member;

collecting the toner and the carrier remaining on said image forming member after the transferring step; and

recycling the collected toner and the carrier for use in the contacting step.

[0015]

The image forming method of the present invention is comprised of: developing an latent image formed on an image forming member with the toner according to the third aspect of a developing member to form a toner image on said image forming member; transferring said toner image to a transfer member; collecting the toner and the carrier remaining on said image forming member after the transferring step; and recycling the collected toner and the carrier for use in the contacting step.

[0016]

It is preferred that the carrier be a small size carrier having a weight average particle diameter of 25-65 μm, more preferably 35-60 μm, most preferably 35-55 μm, it is also preferred that the carrier have such a particle diameter distribution that that portion of the carrier which has a particle diameter of less than 37 μm but no less than 26 μm accounts for 1-60%, more preferably 10-50%, most preferably 15-40%, of a total weight of the carrier for reasons of suitable charging efficiency and prevention of carrier deposition.

[0017]

The carrier thus constructed is combined with a dry toner to form a two-component developer. In general, the toner is used in an amount of 0.5 to 15% by weight based on a total weight of the toner and the carrier. The toner is preferably a small diameter toner having a weight average particle diameter of not greater than 4.0-7.5 μm and such a particle diameter distribution that that portion of the toner having a particle diameter of 5 μm or less accounts for 60-85% based on

a total particle number thereof not only for reasons of obtaining images with good reproducibility and high fidelity but also for the following reasons.

[0018]

It is also preferred that the carrier particles provide an induced magnetic moment of 40-85 emu/g in an applied magnetic field of 1 KOe (1000 Oersteds) for reasons of formation of a magnetic brush having a desired density and prevention of scattering of the carrier particles in the developing device.

[0019]

It is preferred that the carrier having the carbon-containing coating layer have a specific resistance of 10^9-10^{15} $\Omega\cdot$cm for reasons of obtaining satisfactory images. When the specific resistance is excessively high, it is impossible to obtain a high image density because suitable electric field for the development is not established. On the other hand, when the specific resistance is excessively small, the electrostatic latent image is apt to disappear in a case where a strong developing bias is applied. The electric resistance of carrier may be controlled by adjusting the amount of carbon in the resin coating layer and/or the thickness of the resin coating layer.

[0020]

[0021]

Example of coating resin for a carrier core include tetrafluoroethylene resins, monochlorotrifluoroethylene resins,

polyvinylidene fluoride resins, silicone resins, polyester resins, polystyrene resins, polyamide resins, polyvinylbutyral resins, and the like.

[0022]

Silicone resins applicable for the present invention include silicone vanish (e.g. TSR 115, TSR114, TSR 102, TSR 103, YR 3061, TSR 110, TSR 116, TSR 117, TSR 108, TSR 109, TSR 180, TSR 181, TSR 187, TSR 144 and TSR 165 (all products of Toshiba Silicone K. K.), KR 271, KR272, KR275, KR280, KR282, KR 267, KR 272, KR 275, KR 280, KR 282, KR 267, KR269, KR 211 and KR212 (all products of Shinetsu Silicone K. K.)), alkyd-modified silicone vanish (e.g. TSR 184 and TSR 185 (all products of Toshiba Silicone K. K.)), epoxy-modified silicone vanish (e.g. TSR0194 and YS 54 (all products of Toshiba Silicone K. K.)), polyester-modified silicone vanish (e.g. TSR 187 product of Toshiba Silicone K. K.), acryl-modified silicone vanish (e.g. TSR 170 and TSR 171 (all products of Toshiba Silicone K. K.)), urethane-modified silicone vanish (e.g. TSR 175 product of Toshiba Silicone K. K.), reactive silicone resins (e.g. KA 1008, KBE 1003, KBC 1003, KBM 303, KBM 303, KBM 403, KBM 503, KBM 503, KBM 602 and KBM 603 (all products of Shinetsu Silicone K. K.)) and the like.

[0023]

Carbon blacks applicable for the present invention include, for example, furnace black, acetylene black, channel black and the like.

[0024]

As a binder resin for used in toner which is used together with the carrier of the present invention, various thermoplastic resin can be suitably used. Examples of the binder resin include: styrenes such as styrene, per-chlorostyrene; vinyl esters such as vinyl chloride, vinyl bromide, vinyl propionate, vinyl fluoride, vinyl acetate, vinyl benzoate, vinyl butyrate and the like; α-methylene aliphatic monocarboxylic acid esters such as methyl acrylate, ethyl acrylate, n-buyl acrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, methyl α-chloroacrylate, methyl methacrylate, ethyl methacrylate, and the like; acrylonitriles; methacrylonitriles; acrylamides; vinyl ethers such as methyl vinyl ether, isobutyl vinyl ether, ethyl vinyl ether and the like; vinyl ketones such as methyl vinyl ketone, hexyl vinyl ketone, isopropenyl methyl ketone, and the like; N-vynyl compound such as N-vinylpyrrol, N-vinylcarbazole, N-vinylinedole, N-vynylpyrrolidone. The homopolymers and copolymers thereof may be used singly, in combination of two or more thereof or in conjunction with a non-vinyl resin, for example non-vinyl thermoplastics, such as a rosin-modified phenol-formalin resin, an oil-modified epoxy resin, a polyurethane resin, a polyamide resin, a cellulose resin or a polyether resin.

[0026]

Measuring Method

A number average particle diameter of carbon particles located in the coating layer

A coated carrier sample is immersed in a strong acid solution to

dissolve the core material thereof. The sample from which the core material has been removed in sliced by Ultra-Microtome FC4E (manufactured by Nissei Sangyo K. K.) equipped with a cryo-sectioning system. The sliced sample is photographed with an electron microscope H-8000 manufactured by Hitachi Ltd. (magnification: 30,000 to 50,000) at acceleration voltage of 100 kV. The image is analyzed by an image analyzer Luzex 3 manufactured by Nireco Corp. and converted into binary image data. The diameter of a circle having the same area as that of the carbon particle image.

[0027]

Particle diameter distribution of carrier particle

1) Carrier particles are mixed well and 100 g of carrier particles are sampled.
2) The sample is placed on the uppermost sieve of a plurality of stacked sieves which are set on a low tap shaker and whose opening become gradually fine in the direction from the uppermost to the lowermost. (The shaker is the operated for at least 6 minutes, and the aimed shaking time is 8 minutes)
3) After completion of sieving operation, particles on respective sieves are collected by a paint brush and weighed down to 0.1 g sequentially from the uppermost sieve.

The obtained results are counted up to the first place of minority in terms of percentage by weight.

[0028]

Measuring procedure of the magnetic characteristics

1) DC magnetization characteristic automatic recording device

("TYPE-3257-36", made by Yokokawa Hokushin Denki Co.)

2) Electromagnet magnetizer ("TYPE-3261-15", made by Yokokawa Hokushin Denki Co.)

3) Pickup coil (Bi & H coil, "TYPE-3261-20", made by Yokokawa Hokushin Denki Co.)

4) Sample cell (made of acrylic resin)

5) Electric balance, minimum graduation: 1 mg

[0029]

Measuring method of specific resistance of carrier

A cell A shown in FIG. 3 is charged with a carrier sample; the electrodes 1 and 2 are connected so as to contact with the sample; and a voltage is applied between the electrodes. The current running is measured, and a specific resistance is calculated therefrom. Note that, in this method, a specific resistance may vary due to a variation in a loading factor of the carrier as the carrier consists of particles. The conditions for measuring method are as follow: the contact area between the sample and each electrode is about 4.0 cm2; the thickness of the sample is about 2 mm; and a load of the upper electrode 2 is 275 g; and the applied voltage is 500 V.

[0030]

Measuring method of particle diameter distribution of toner

The particle diameter distribution of the toner is measured with a Coulter counter TA-II or a Coulter Multisizer II (both manufactured by Coulter Electronics, Inc.). The measuring method is described below.

An an electrolytic solution for measurement, an aqueous 1% by weight NaCl solution of first-grade sodium chloride is used. Measurement is

carried out by adding, as a dispersant, 0.1-5 ml of a surfactant (alkylbenzenesulfonic acid salt) to 100 to 150 ml of the above electrolytic solution, and further adding 2 to 20 mg of a sample to be measured. The resulting mixture is subjected to dispersion for about 1 minute to about 3 minutes in an ultrasonic dispersing machine. Using an aperture of 100 μm in the above particle size distribution measuring device, the particle size distribution is measured on the basis of the number and volume with the Coulter counter for particles having a diameter in the range of 2-40.30 μm to determine the number average particle diameter and volume average particle diameter of the toner. The following 13 channels are used: 2.00 to less than 2.52; 2.52 to less than 3.17; 3.17 to less than 4.00; 4.00 to less than 5.04; 5.04 to less than 6.35; 6.35 to less than 8.00; 8.00 to less than 10.08; 10.08 to less than 12.70; 12.70 to less than 16.00; 16.00 to less than 20.20; 20.20 to less than 25.40; 24.50 to less than 32.00; 32.00 to less than 40.30.

[0031]

Measuring method of number average molecular weight of toner

The number average molecular weight Mn of toner is measured by gel permeation chromatography (GPC) under the following conditions:

Device: GPC-150C (manufactured by Waters Inc.)

Column: KF801-807 (manufactured by Showdex Inc.)

Temperature: 40 °C.

Solvent: THF (tetrahydrofuran)

Elution rate: 1.0 mL/minute

Sample: 0.1 ml of the sample having a concentration of 0.05-0.6%

Using a molecular weight calibration curve drafted from a

monodispersed polystyrene standard as a calibration, a number average molecular weight Mn of the toner is calculated from the molecular weight distribution of toner binder measured by the aforementioned conditions.

[0032]

[Embodiments]

The present invention will be described in further detail with reference to several examples and comparative examples below, each of which is not intended to limit the scope of the present invention.

Note that the amount (part) of each component in the Examples is part by weight.

[0033]

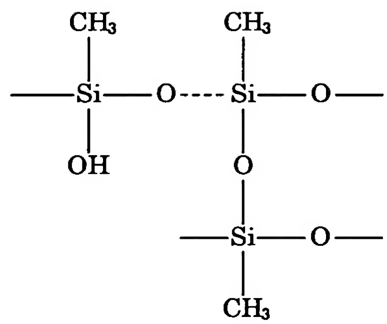
Preparation of Coating Liquid a for Carrier

Dimethylsilicone resin having constituting units of the formula (1) below (toluene solution, solid matter: 20%)	600 parts
Toluene	600 parts
γ-aminotriethoxysilane (KBE 903 manufactured by Sin-Etsu Chemical Co., Ltd.)	9.7 parts
Carbon black (BP-2000, manufactured by Cabot Company Ltd.)	10.2 parts

The above components were mixed and thoroughly dispersed with a homomixer (jacket temperature: 35-40°C) for 20 minutes to obtain Coating Liquid a.

[0034]

[Chemical Formula 1]



[0035]

Preparation of Coating Liquid b for Carrier

Dimethylsilicone resin used for Coating Liquid a (toluene solution, solid matter: 20%)	600 parts
Toluene	600 parts
γ-aminotriethoxysilane (KBE 903 manufactured by Sin-Etsu Chemical Co., Ltd.)	9.7 parts
Carbon black (BP-2000, manufactured by Cabot Company Ltd.)	10.2 parts

The above components were mixed and thoroughly dispersed with a homomixer (jacket temperature: 35-40°C) for 5 minutes to obtain Coating Liquid b.

[0036]

Example 1

Preparation of Small Size Carrier A

Carrier Core A	5000 parts
Coating Liquid a	1220 parts
Tin catalyst [$(C_3H_7)_2Sn(OCOCH_3)_2$ 10% toluene solution]	16.8 parts

The above carrier core was placed on a rotary bottom disc of a fluidized bed of a coating device. The disc was rotated from a vortex. When

the vortex was stabilized, Coating Liquid a was sprayed into the vortex, thereby coating the carrier core. The resulting coated carrier was heated at 300°C. for 2 hours in an electric oven to obtain Carrier A having a specific resistance of 2.0×10^{13} Ω·cm.

[0037]

[Table 1]

	Particle diameter distribution μm(%)								D
	+105	~75	~63	~44	~37	~25	-25		μm
A	tr	0.3	3.0	64.5	16.7	15.5			48
B	tr	1.0	6.0	63.1	18.2	11.7			50

	Electric characteristics			Magnetic characteristics					Particle characteristics	
	Resistance Ωcm			Saturation magnetization	σ1000	σ500	Residual magnetization	Holding	Bulk density	Fluidity
	100V	500V	1000V	emu/g	emu/g	emu/g	G	Oe	g/cm³	Sec/50g
A				91.4	78.5	58.4	80.0	12.5	2.63	27.2
B				65.5	60.1	54.2	tr	tr	2.48	27.9

Note that "D" in the above table denotes an average particle diameter.

[0038]

Example 2

Preparation of Small Size Carrier B

Carrier Core B 5000 parts

Coating Liquid a 1220 parts

Tin catalyst [$(C_3H_7)_2Sn(OCOCH_3)_2$ 10% toluene solution] 16.8 parts

The above carrier core was placed on a rotary bottom disc of a fluidized bed of a coating device. The disc was rotated from a vortex. When

the vortex was stabilized, Coating Liquid a was sprayed into the vortex, thereby coating the carrier core. The resulting coated carrier was heated at 300°C. for 2 hours in an electric oven to obtain Carrier A having a specific resistance of 4.43 $\times 10^{13}$ Ω·cm.

[0039]

Preparation of Small Size Toner

Polyester resin A (acid value: 27.1 mg KOH/g, softening point: 147.2°C., Tg: 60.4°C., THF insoluble: 27.1% by weight)	60 parts
Polyester resin B (acid value: 9.5 mg KOH/g, softening point: 100.2°C., Tg: 62.4°C., THF insoluble: 0% by weight)	40 parts
Carnauba wax (melting point: 82°C., acid value: 2)	3 parts
Carbon black (trade name as #44, manufactured by Mitsubishi Chemical Corp.)	8 parts
Chromium-containing manoazo complex	3 parts

The above components were mixed using a Henschel mixer. The mixture was heated at a temperature of from 130 to 140°C. and kneaded for about 30 minutes using a roll mill. The kneaded mixture was cooled, pulverized using a jet mill and classified. The thus obtained mother toner had a number average molecular weight Mn of 2,600 and such a molecular weight distribution that that portion of the toner having a molecular weight of 1,000 or less accounts for 42% based on a total molecular number thereof. To the mother toner particles (100 parts), 1.5 parts of hydrophonic silica (R972 manufactured by Nihon Aerosil Inc.) as an external additive, mixed using Henschel mixer and classified to remove large particles, thereby obtaining a toner. The thus obtained toner was subjected to the measurement by Coulter

counter TA-II, in which the aperture was set to 100 μm. The results are shown in Table 2. The weight average particle diameter was 5.7 μm.

[0040]

[Table 2]

Channel	Diameter range		Number of particles	Number distribution	Volume distribution
1	1.26	1.59	0	0.00	0.00
2	1.59	2.00	0	0.00	0.00
3	2.00	2.52	2045	6.82	0.68
4	2.52	3.17	3390	11.30	2.26
5	3.17	4.00	6913	23.04	9.23
6	4.00	5.04	8704	29.01	23.25
7	5.04	6.35	6509	21.70	34.77
8	6.35	8.00	2135	7.12	22.81
9	8.00	10.1	285	0.95	6.09
10	10.1	12.7	17	0.06	0.73
11	12.7	16.0	2	0.01	0.17
12	16.0	20.2	0	0.00	0.00
13	20.2	25.4	0	0.00	0.00
14	25.4	32.0	0	0.00	0.00

D1: 4.4 μm

D4: 5.7 μm

[0041]

4 parts of Toner obtained above and 96 parts of Carrier obtained above were thoroughly mixed with a Turbler (Model T2C) mixer to obtain a two-component developer. The developer thus obtained was charged in a developing device of a copying machine (IMAGIO MF4570 manufactured by Ricoh Company, Ltd.) so as to evaluate an image formed thereby. A total amount of the carrier charged in the developing device was 480 g. The durability test was carried out under the following conditions.

Apparatus Potential Control: Charging potential -950 V, Development potential -600 V, Exposure potential -150 V

Gap Control: doctor gap = gap between sleeve and photoconductor drum =

0.4 mm

Production of Copies: Chart having image area of 6% (A4) 1,000 sheets

Black solid image (A3) 20 sheets

Trim image (A3) 3 sheets

Chart for evaluating image quality (A3) 3 sheets

The durability test was carrier out by making 300k sheets of copies according to the above described details. The results are summarized in Table 3 and FIG. 1. FIG. 1 shows a toner concentration (TC) and a change of Q/M.

[0042]

[Table 3]

Number of copy (k)	Toner concentration (%)	Q/M (μC/g)	Rank of Background Stain
0	4.18	32.1	4.5
30	4.40	32.4	4
60	4.64	32.1	4
90	4.64	32.1	4
120	7.54	21.7	3
150	8.52	18.6	2
180			
210			
240			
270			
300			

[0043]

As will be appreciated from the results shown in Table 3 and FIG. 1, when about 100k copies are produced, background stains are significant. The scattering of toner became significant inside the copying machine after production of 150k copies, and thus the durability test was suspended. The amount of the carrier after production of 150k copies was fount to be less than 400 g.

A considerable increase of the toner concentration is presumably

attributed to a decrease of the carrier deposition due to deposition thereof which may have caused an erroneous operation of the toner concentration sensor of the copying machine, thereby supplying a toner in an amount of more than sufficient.

During the initial stage of produced images, the technical features of a small size toner was obtained, and the high quality images having high gradation and resolution were obtained.

[0044]

Example 4

Preparation of Carrier A

Carrier Core A	5000 parts
Coating Liquid a	1220 parts
Tin catalyst [$(C_3H_7)_2Sn(OCOCH_3)_2$ 10% toluene solution]	16.8 parts

The above carrier core was placed on a rotary bottom disc of a fluidized bed of a coating device. The disc was rotated from a vortex. When the vortex was stabilized, Coating Liquid a was applied to the core by Coating Device (the internal temperature: 70°C), thereby coating the carrier core. The resulting coated carrier was heated at 300°C. for 2 hours in an electric oven to obtain Carrier A.

[0045]

[Table 4]

	Particle diameter distribution μm(%)								D
	+105	~75	~63	~44	~37	~25	-25		μm
A	tr	5.5	58.7	34.5	1.3				48
B	tr	0.3	3.0	64.5	16.7	15.5			50

	Electric characteristics			Magnetic characteristics					Particle characteristics	
	Resistance Ωcm			Saturation magnetization	σ1000	σ500	Residual magnetization	Holding	Bulk density	Fluidity
	100V	500V	1000V	emu/g	emu/g	emu/g	G	Oe	g/cm³	Sec/50g
A				64	59	51	tr	Tr	2.79	23.1
B				91.4	78.5	58.4	80.0	12.5	2.63	27.2

[0046]

Example 5

Preparation of Carrier B

Carrier Core B 5000 parts

Coating Liquid a 1220 parts

Tin catalyst [$(C_3H_7)_2Sn(OCOCH_3)_2$ 10% toluene solution] 16.8 parts

The above carrier core was placed on a rotary bottom disc of a fluidized bed of a coating device. The disc was rotated from a vortex. When the vortex was stabilized, Coating Liquid a was applied to the core by Coating Device (the internal temperature: 70°C), thereby coating the carrier core. The resulting coated carrier was heated at 300°C. for 2 hours in an electric oven to obtain Carrier B.

[0047]

Example 6

Preparation of Carrier C

Carrier Core A 5000 parts

Coating Liquid a 1220 parts

Tin catalyst [$(C_3H_7)_2Sn(OCOCH_3)_2$ 10% toluene solution] 16.8 parts

The above carrier core was placed on a rotary bottom disc of a fluidized bed of a coating device. The disc was rotated from a vortex. When

the vortex was stabilized, Coating Liquid a was applied to the core by Coating Device (the internal temperature: 100°C), thereby coating the carrier core. The resulting coated carrier was heated at 300°C. for 2 hours in an electric oven to obtain Carrier C.

[0048]

Example 7

Preparation of Carrier D

Carrier Core A	5000 parts
Coating Liquid b	1220 parts
Tin catalyst [$(C_3H_7)_2Sn(OCOCH_3)_2$ 10% toluene solution]	16.8 parts

The above carrier core was placed on a rotary bottom disc of a fluidized bed of a coating device. The disc was rotated from a vortex. When the vortex was stabilized, Coating Liquid a was applied to the core by Coating Device (the internal temperature: 70°C), thereby coating the carrier core. The resulting coated carrier was heated at 300°C. for 2 hours in an electric oven to obtain Carrier D.

[0049]

Example 8

4 parts of Toner obtained in Example 3 and 96 parts of Carrier A obtained in Example 4 were thoroughly mixed with a Turbler (Model T2C) mixer to obtain a two-component developer. 500 g of the thus obtained developer was charged in a developing device for a copying machine (IMAGIO MF4570 manufactured by Ricoh Company, Ltd.) and tested for the image quality thereof. The results are summarized in Table 5.

[0050]

Example 9

4 parts of Toner obtained in Example 3 and 96 parts of Carrier B obtained in Example 5 were thoroughly mixed with a Turbler (Model T2C) mixer to obtain a two-component developer. 500 g of the thus obtained developer was charged in a developing device for a copying machine (IMAGIO MF4570 manufactured by Ricoh Company, Ltd.) and tested for the image quality thereof. The results are summarized in Table 5.

[0051]

Comparative Example 1

4 parts of Toner obtained in Example 3 and 96 parts of Carrier C obtained in Example 6 were thoroughly mixed with a Turbler (Model T2C) mixer to obtain a two-component developer. 500 g of the thus obtained developer was charged in a developing device for a copying machine (IMAGIO MF4570 manufactured by Ricoh Company, Ltd.) and tested for the image quality thereof. The results are summarized in Table 5.

[0052]

Comparative Example 2

4 parts of Toner obtained in Example 3 and 96 parts of Carrier D obtained in Example 7 were thoroughly mixed with a Turbler (Model T2C) mixer to obtain a two-component developer. 500 g of the thus obtained developer was charged in a developing device for a copying machine (IMAGIO MF4570 manufactured by Ricoh Company, Ltd.) and tested for the image quality thereof. The results are summarized in Table 5.

[0053]

[Table 5]

	Number average particle diameter of carbon (μm)	Specific resistance of carrier (Ω·cm)	Image Density	Rank of reproducibility of fine line image	Others
Ex. 1	0.04	2.0×10^{13}	1.41	4	
Ex. 2	0.04	1.5×10^{13}	1.45	5	
Com. Ex, 1	0.007	7.9×10^{13}	1.19	4	Edge effect
Com. Ex. 2	0.16	5.0×10^{13}	1.50	3	White spots

[0054]

Example 10

The PCU of the copying machine was modified so as not to vary the amount of the carrier in the developing device due to carrier deposition.

The theory of the modification of the PCU was as follow. The PCU of IMAGIO MF4580 was equipped with a toner recycling system which scraped and collected the toner remained on the photoconductor by a cleaning blade, and transported the collected toner to the developing device through a transportation path in the PCU. By efficiently utilizing this system, the carrier induced carrier deposition was transported to the developing device. In the toner recycling system before the modification, the carrier attached to a latent image bearing part was transported together with a toner up to the cleaning unit. However, the carrier scraped by the cleaning blade was collected about the blade, and eventually the collected carrier was slipped from the photoconductor and scatted inside the machine.

The present inventors have been found that it is effective to dispose a fur brush in front of the blade (rotating direction of the fur brush was set to the opposite rotating direction of the photoconductor) so as to transport the carrier caused carried deposition to the transportation path for recycling which located behind the cleaning blade. (but, any means can be utilized if a

similar effect is obtained).

IMAGIO MF4570 was equipped with the modified PCU, 500 g of the development which was comprised of the toner obtained in Example 3 and the carrier was charged therein, and durability test was carrier out. The results are summarized in Table 6 and FIG. 2.

[0055]

[Table 6]

Number of copy (k)	Toner concentration (%)	Q/M (μC/g)	Rank of Background Stain
0	4.13	30.6	4.5
30	3.95	29.0	4.5
60	4.41	23.2	4
90	3.90	27.2	4
120	4.44	25.8	4
150	3.76	33.0	4
180	4.44	29.5	4
210	3.92	33.3	4
240	4.11	31.7	4
270	4.04	32.9	4
300	4.05	33.5	4

[0056]

As will be appreciated from the results shown in Table 6 and FIG. 2, the toner concentration was stable, no background stain was observed and productions of stable image were obtained thoughout the reproduction of 300k copies. At the time the durability test was finished, the developing device was removed from the copying machine for observation of inside the machine, but toner scattering was observed The amount of the carrier in the developing device was found to be less than 478 g, and no significant change in amount was not found. From the fact that only small amount of the carrier was found in the transportation path, it is assumed that the stable durability and reliability were obtained, tough carrier deposition was occurred, as a

result of a suitable operation of a carrier recycle system.

In addition, the images having high gradation and resolution was obtained throughout the test, and the improved images due to the small size toner were maintained.

[0057]

Example 11

4 parts of Toner obtained in Example 3 and 96 parts of Carrier B obtained in Example 2 were thoroughly mixed with a Turbler (Model T2C) mixer to obtain a two-component developer. 500 g of the thus obtained developer was charged in a developing device for a copying machine (IMAGIO MF4570 manufactured by Ricoh Company, Ltd.) and tested for the image quality thereof. In this test, the PCU having carrier recycle system of Example 10 was used. Throughout the test, the toner concentration was stable, background stain and toner scattering were prevented, and high quality images were obtained, all of which may be attributed to an operation of carrier recycle system.

[0058]

[Effects of the Invention]

In accordance with the invention defined in Claim 1, it is provided a developer capable of forming an image having high image density and excellent line image reproducibility.

In accordance with the invention defined in Claims 2 to 4, it is provided a carrier for an image developer for electrophotography, inhibiting problems related to carrier depositions and maintaining stable quality in terms of electric resistance in spite of its small particle size, a toner containing

such carrier, and image forming method using such toner, especially the image forming method wherein a total amount of carrier in a developing device is maintained at a certain level.

[Brief Description of the Drawings]

[FIG. 1]

FIG. 1 shows graphs illustrating a relationship between the toner concentration and a relationship between Q/M in the durability test (Prior Art).

[FIG. 2]

FIG. 2 shows graphs illustrating a relationship between the toner concentration and a relationship between Q/M in the durability test.

[FIG. 3]

FIG. 3 is a cross-sectional view diagrammatically illustrating a device used for measuring electric resistance of carrier particles.

[Description of the Reference Numerals]

1: lower electrode

2: upper electrode

4: amplifier

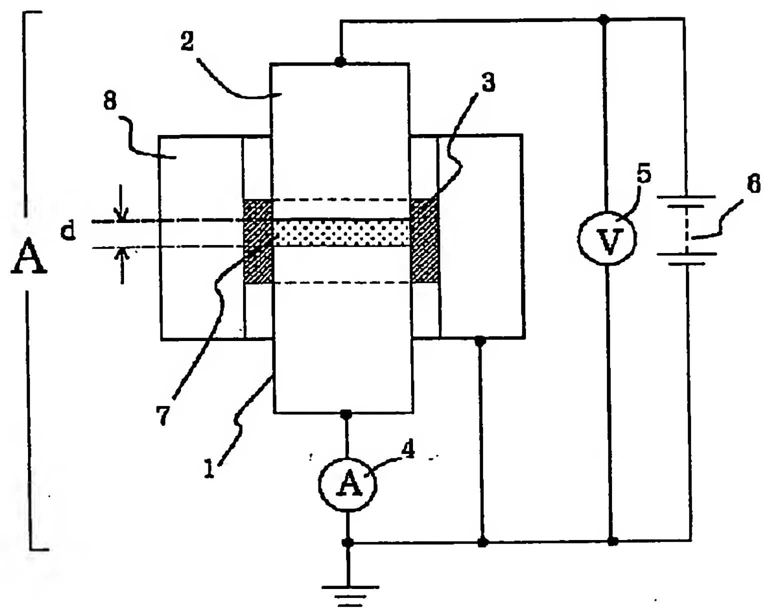
5: voltmeter

6: voltage source

7: carrier sample

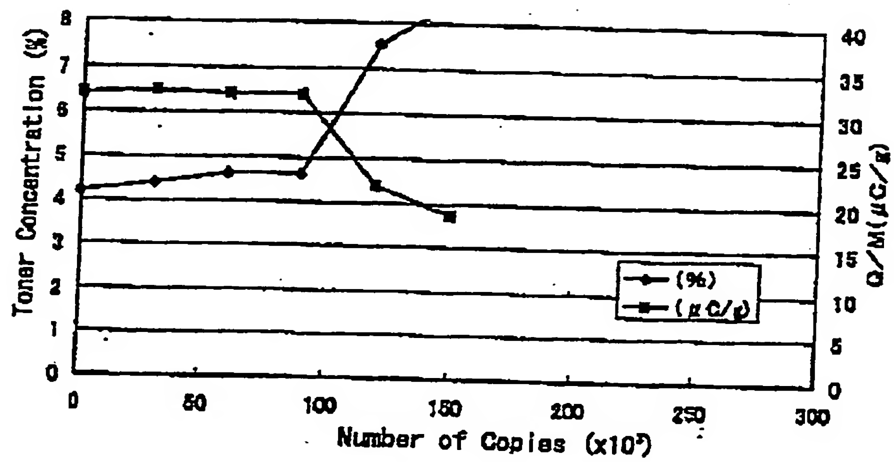
8: cell holder

[FIG. 3]

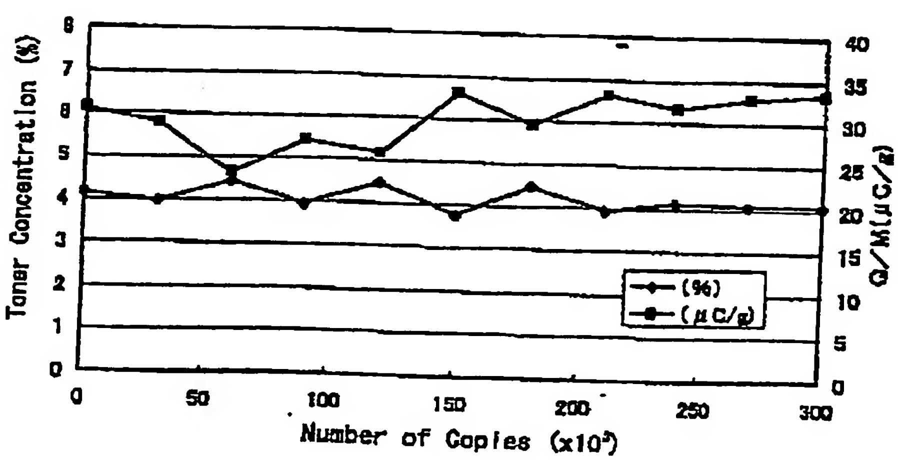


[Document Name] Drawings

[FIG. 1]



[FIG. 2]



[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

[ABSTRACT]

[OBJECT]

To provide a carrier for an image developer for electrophotography, inhibiting problems related to carrier depositions in spite of its small particle size, and maintaining stable quality in terms of electric resistance.

[SOLVING MEANS]

A carrier for an image developer for electrophotography, which contains a coating layer including at least a coating resin and carbon particles having a number average particle size of 0.01-0.1 μm.

[SELECTED FIGURE] None